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H.H. NELSON

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# REACTION CHEMISTRY OF BORON HYDRIDES

H. H. Nelson  
Chemistry Division  
Naval Research Laboratory  
Washington, DC 20375

We have recently begun a program on Boron Combustion Chemistry in the Chemistry Division at NRL. Our initial efforts have involved investigations of the room temperature reactions of  $\text{BH}_3$  [1] and  $\text{BH}$  [2] with various oxidants and hydrocarbons. In conjunction with the gas-phase experimental work, we are pursuing a computational study of the heats of formation of boron compounds and reaction energetics. In addition, there is a component of the program emphasizing the heterogeneous chemistry of boron oxides.

$\text{BH}_3$  is produced by the 193 nm photolysis of  $\text{BH}_3\text{CO}$  or  $\text{B}_2\text{H}_6$ .  $\text{BH}$  is only observed after  $\text{BH}_3\text{CO}$  photolysis, not from  $\text{B}_2\text{H}_6$ .  $\text{BH}_3$  is probed by monitoring time resolved IR absorption in the Q-branch of the  $\nu_2$  band near  $1140\text{ cm}^{-1}$  using a tunable diode laser. Most experiments were performed with  $\text{B}_2\text{H}_6$  as the photolytic precursor because of less spectral congestion in the IR. A schematic diagram of the apparatus used for  $\text{BH}_3$  measurements is shown in Figure 1. The  $\text{BH}$  experiments are carried out in a more conventional laser photolysis/laser induced fluorescence apparatus in which  $\text{BH}$  is probed by exciting fluorescence in the  $\text{A}^1\Pi \leftrightarrow \text{X}^1\Sigma^+$  system near 430 nm.

We find the association reaction of  $\text{BH}_3$  with  $\text{CO}$  to be in the intermediate pressure regime over the pressure range studied (10-620 Torr,  $\text{N}_2$ ) with rate constants ranging from  $1.5$  to  $47 \times 10^{-13}\text{ cm}^3\text{ s}^{-1}$ . For  $\text{BH}_3 + \text{NO}$ , the rate constant approaches the high-pressure limit of  $3.7 \times 10^{-13}\text{ cm}^3\text{ s}^{-1}$  at pressure  $\approx 200$  Torr  $\text{N}_2$ . The pressure-independent rate constant ( $P \geq 6$  Torr) for the reaction of  $\text{BH}_3 + \text{C}_2\text{H}_4$  is  $(5.2 \pm 1.0) \times 10^{-11}\text{ cm}^3\text{ s}^{-1}$ . For the reactions  $\text{BH}_3$  with  $\text{O}_2$  and  $\text{H}_2\text{O}$  we are able to place upper limits of  $5 \times 10^{-15}$  and  $6 \times 10^{-15}\text{ cm}^3\text{ s}^{-1}$ , respectively, on the reaction rate constants.

Room temperature reactions of  $\text{BH}$  are primarily pressure-independent in the 5 to 1000 Torr pressure range. The rate constants derived from our measurements are listed in Table 1.

TABLE 1: Room-Temperature Rate Constants for  $\text{BH}$  Reactions

Reaction	k ( $\text{cm}^3\text{ s}^{-1}$ )
$\text{BH} + \text{NO}$	$(1.35 \pm 0.03) \times 10^{-10}$
$\text{BH} + \text{H}_2\text{O}$	$(9.76 \pm 0.40) \times 10^{-12}$
$\text{BH} + \text{O}_2$	$(8.08 \pm 0.09) \times 10^{-13}$
$\text{BH} + \text{CO}_2$	$(2.64 \pm 0.07) \times 10^{-14}$
$\text{BH} + \text{C}_2\text{H}_4$	$(1.17 \pm 0.02) \times 10^{-10}$
$\text{BH} + \text{TME}^a$	$(1.87 \pm 0.07) \times 10^{-10}$

a) 2,3 dimethyl-2-butene



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We have also studied the reaction of BH with H<sub>2</sub> and are able to measure the pressure dependence of this reaction over the range 10-700 Torr (see Figure 2) and extract the following kinetic parameters:  $k_0 = (1.05 \pm 0.11) \times 10^{-31} \text{ cm}^6 \text{ s}^{-1}$ ,  $k_{\infty} = (3.52 \pm 0.42) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ , and  $F_c = 0.51 \pm 0.06$ . The reaction of BH with CO is in the transition region at these pressures with the rate constant ranging from  $3.9$  to  $58 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ .

Mechanistic details inferred from these measurements and our plans for further work in this field will be discussed.

#### References:

1. L. Pasternack, R.J. Balla, and H.H. Nelson, "Study of Reactions of BH<sub>3</sub> with CO, NO, O<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, and H<sub>2</sub>O Using Diode Laser Absorption". J. Phys. Chem., **92**, 1200 (1988).
2. J.K. Rice, N.J. Caldwell, and H.H. Nelson, "The Gas-Phase Reaction Kinetics of BH", manuscript in preparation.

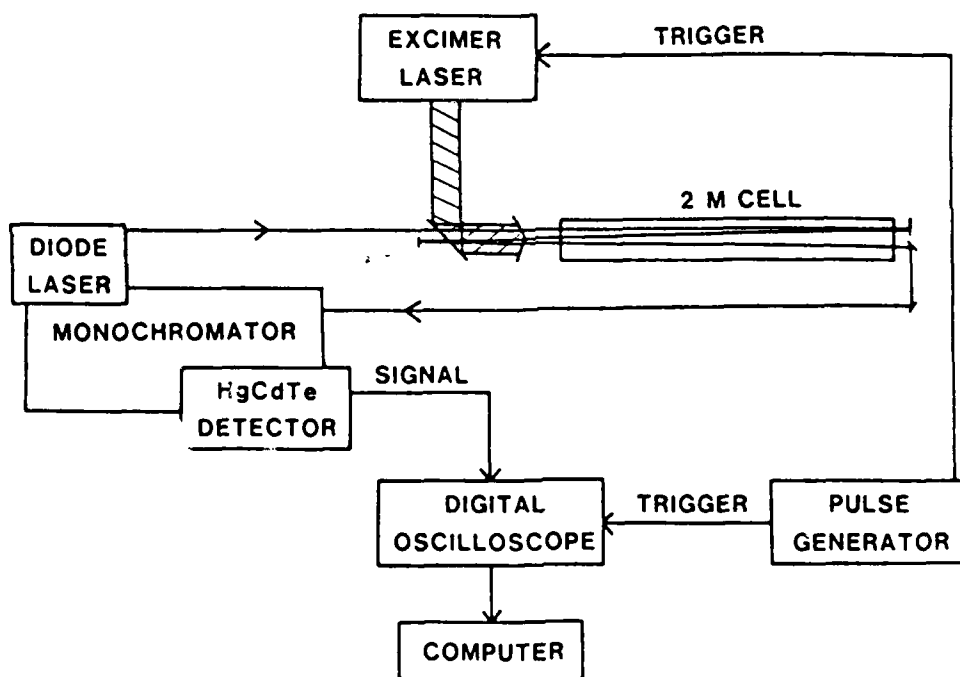


Figure 1. Schematic diagram of the apparatus used to study BH<sub>3</sub> reactions.

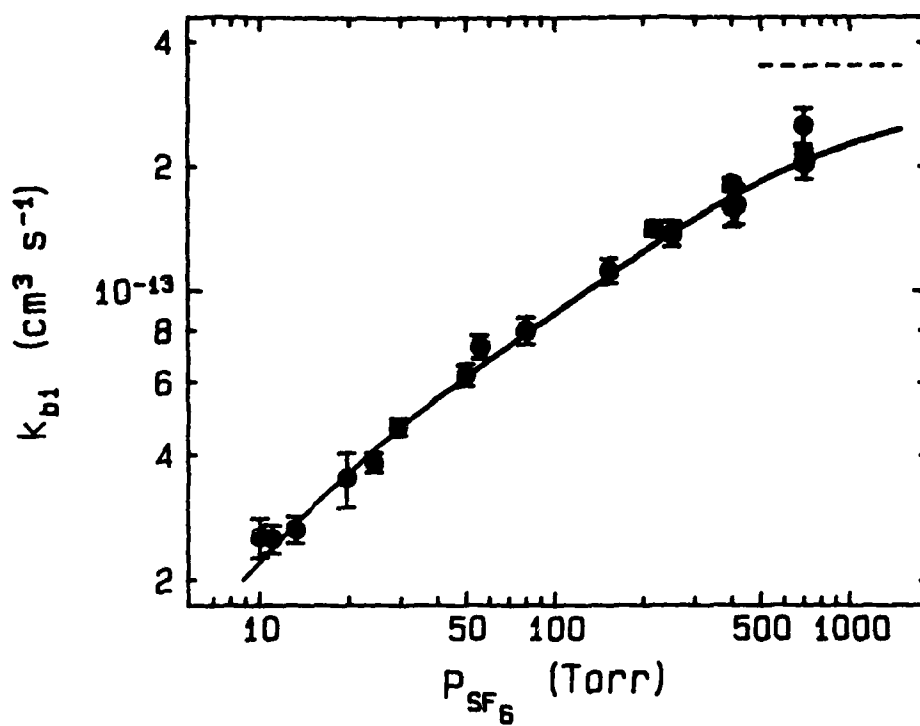


Figure 2. Observed pressure dependence for the reaction  $\text{BH} + \text{H}_2$  at room temperature. The solid line is a fit to the data using parameters given in the text. The dashed line is the fitted high pressure limit.